

# A Symmetry-Adapted Algebraic Approach to Molecular Spectroscopy

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## 1 Introduction

The study of molecular vibrational spectra [1] requires theoretical models in order to analyze and interpret the measurements. These models range from simple parametrizations of the energy levels, such as the Dunham expansion [2], to *ab initio* calculations, where solutions of the Schrödinger equation in different approximations are sought [3, 4, 5, 6]. In general, the latter involve the use of internal coordinates and the evaluation of force field constants associated to derivatives at the potential minima. While this method can be reliably applied to small molecules [7], it quickly becomes a formidable problem in the case of larger molecules, due to the size of their configuration spaces. New calculational tools to describe complex molecules are thus needed.

In 1981 an algebraic approach was proposed to describe the roto-vibrational structure of diatomic molecules [8], subsequently extended to linear tri- and four- atomic molecules [9] and certain non-linear triatomic molecules [10]. Although these were encouraging results, the model could not be extended to polyatomic molecules, due to the impossibility of incorporating the underlying discrete symmetries. This difficulty could be surmounted by treating the vibrational degrees of freedom separately from the rotations. In 1984 Van Roosmalen *et al.* proposed a  $U(2)$  based model to describe the stretching vibrational modes in ABA molecules [11] which was later extended to describe the stretching vibrations of polyatomic molecules such as octahedral and benzene like molecules [12]. Recently the bending modes have also been included in the framework, which was subsequently applied to describe  $C_{2v}$ -triatomic molecules [13] and the lower excitations of tetrahedral molecules [14], using a scheme which combines Lie-algebraic and point group methods. In a different approach, it has also been suggested [15] to use a  $U(k+1)$  model for the  $k = 3n - 3$  rotational and vibrational degrees of freedom of a  $n$ -atomic molecule. This model has the advantage that it incorporates all rotations and vibrations and takes into account the relevant point group symmetry, but for larger molecules the number of possible interactions and the size of the Hamiltonian matrices increase very rapidly, making it impractical to apply.

Although the algebraic formulations have proved useful, several problems remained, most important of which is the absence of a clear connection to traditional methods. On the other hand, a related problem is the lack of a systematic procedure to construct all physically meaningful interactions in the algebraic space. In this paper we show that both these issues can be resolved by considering a symmetry-adapted version of the  $U(2)$  algebraic model for the analysis of molecular vibrational spectra. In this approach it is possible to construct algebraic operators with well defined physical meaning, in particular interactions fundamental for the description of the degenerate modes present in systems exhibiting high

degree of symmetry. The procedure to construct them takes full advantage of the discrete symmetry of the molecule and gives rise to all possible terms in a systematic fashion, providing a clear-cut connection between the algebraic scheme and the traditional analyses based on internal coordinates, which correspond to the harmonic limit of the model [16].

As a test of the symmetry-adapted approach we discuss an application to three  $\mathcal{D}_{3h}$ -triatomic molecular systems, namely  $\text{H}_3^+$ ,  $\text{Be}_3$  and  $\text{Na}_3^+$ , and to two tetrahedral molecules, the  $\text{Be}_4$  cluster and the methane molecule. Since small molecules can in general be well described by means of *ab initio* calculations [17, 18], we emphasize the basic purpose of this work. We establish an exact correspondence between configuration space and algebraic interactions by studying the harmonic limit of the  $U(2)$  algebra. This general procedure not only allows to derive algebraic interactions from interactions in configuration space, but can also be applied to cases for which no configuration space interactions are available. The  $\mathcal{D}_{3h}$ -triatomic molecules constitute the simplest systems where degenerate modes appear and where the new interactions in the model become significant. In the case of  $\text{Be}_4$  we present a comparison with *ab initio* calculations, while for  $\text{CH}_4$  we present a detailed comparison with experiment. The application of these techniques to other molecules, as well as a more complete presentation can be found in references [16, 19, 20, 21].

## 2 The $U(2)$ vibron model

The model is based on the isomorphism of the  $U(2)$  Lie algebra and the one dimensional Morse oscillator

$$\mathcal{H} = -\frac{\hbar^2}{2\mu} \frac{d^2}{dx^2} + D(e^{-2x/d} - 2e^{-x/d}) , \quad (1)$$

whose eigenstates  $\mathcal{E}$  can be associated with  $U(2) \supset SO(2)$  states [22]. In order to see how this isomorphism comes about, consider the radial equation

$$\frac{1}{2} \left( -\frac{1}{r} \frac{d}{dr} r \frac{d}{dr} + \frac{\sigma^2}{r^2} + r^2 \right) \phi(r) = (N+1) \phi(r) , \quad (2)$$

which corresponds to a two-dimensional harmonic oscillator (in units where  $\hbar = \mu = e = 1$ ) associated to a  $U(2)$  symmetry algebra [23]. By carrying out a change of variable

$$r^2 = (N+1)e^{-\rho} ,$$

Eq. (2) transforms into

$$\left[ -\frac{d^2}{d\rho^2} + \left( \frac{N+1}{2} \right)^2 (e^{-2\rho} - 2e^{-\rho}) \right] \phi(\rho) = -\left( \frac{\sigma}{2} \right)^2 \phi(\rho) . \quad (3)$$

This can be identified with Eq. (1) after defining  $x = \rho d$  and multiplying by  $\hbar^2/2\mu d^2$ , provided that

$$D = \frac{\hbar^2}{8\mu d^2} (N+1)^2 , \quad (4)$$

$$\mathcal{E} = -\frac{\hbar^2}{2\mu d^2} m^2 , \quad (5)$$

where we have defined  $m = \sigma/2$ . In the framework of the  $U(2)$  algebra, the operator  $\hat{N}$  corresponds to the total number of bosons and is fixed by the potential shape according to Eq. (4), while  $m$ , the eigenvalue of the  $SO(2)$  generator  $J_z$ , takes the values  $m = \pm N/2, \pm(N-2)/2, \dots$ . The Morse spectrum is reproduced twice and consequently for these applications the  $m$ -values must be restricted to be positive. In terms of the  $U(2)$  algebra, it is clear from Eqs. (3-5) that the Morse Hamiltonian has the algebraic realization

$$\hat{H} = -\frac{\hbar^2}{2\mu d^2} \hat{J}_z^2 = -A \hat{J}_z^2 . \quad (6)$$

In addition, the  $U(2)$  algebra includes the raising and lowering operators  $\hat{J}_+$  and  $\hat{J}_-$ , which connect different energy states, while the angular momentum operator is given by  $\hat{J}^2 = \hat{N}(\hat{N} + 2)/4$ , as can be readily shown.

The Morse Hamiltonian of Eq. (6) can be rewritten in the more convenient form

$$\hat{H}' = \hat{H} + A \frac{\hat{N}^2}{4} = \frac{A}{2}[(\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+) - \hat{N}] , \quad (7)$$

where we have used the relation  $\hat{J}_z^2 = \hat{J}^2 - (\hat{J}_+ \hat{J}_- + \hat{J}_- \hat{J}_+)/2$  and added a constant term  $A\hat{N}^2/4$  in order to place the ground state at zero energy. The parameters  $N$  and  $A$  are related to the usual harmonic and anharmonic constants  $\omega_e$  and  $x_e\omega_e$  used in spectroscopy. To obtain this relation it is convenient to introduce the quantum number

$$v = \frac{N}{2} - m , \quad (8)$$

which corresponds to the number of quanta in the oscillator. In terms of  $v$ , the corresponding energy expression takes the form

$$E' = -A(m^2 - \frac{N^2}{4}) = -\frac{A}{2}(N + 1/2) + A(N + 1)(v + 1/2) - A(v + 1/2)^2 , \quad (9)$$

from which we immediately obtain

$$\begin{aligned} \omega_e &= A(N + 1) , \\ x_e\omega_e &= A . \end{aligned} \quad (10)$$

Thus, in a diatomic molecule the parameters  $A$  and  $N$  can be determined by the spectroscopic constants  $\omega_e$  and  $x_e\omega_e$ .

We now consider the  $U_i(2) \supset SU_i(2) \supset SO_i(2)$  algebra, which is generated by the set  $\{\hat{G}_i\} \equiv \{\hat{N}_i, \hat{J}_{+,i}, \hat{J}_{-,i}, \hat{J}_{0,i}\}$ , satisfying the commutation relations

$$[\hat{J}_{0,i}, \hat{J}_{\pm,i}] = \pm \hat{J}_{\pm,i} , \quad [\hat{J}_{+,i}, \hat{J}_{-,i}] = 2\hat{J}_{0,i} , \quad [\hat{N}_i, \hat{J}_{\mu,i}] = 0 , \quad (11)$$

with  $\mu = \pm, 0$ . As mentioned before, for the symmetric irreducible representation  $[N_i, 0]$  of  $U_i(2)$  one can show that the Casimir operator is given by  $\vec{J}_i^2 = \hat{N}_i(\hat{N}_i + 2)/4$  [23], from which follows the identification  $j_i = N_i/2$ . The  $SO_i(2)$  label is denoted by  $m_i$ .

### 3 The Be<sub>4</sub> cluster

As a specific example, we consider the Be<sub>4</sub> cluster, which has a tetrahedral shape.  $\mathcal{D}_{3h}$  molecules can be similarly treated. In the Be<sub>4</sub> case there are six  $U_i(2)$  algebras involved ( $i = 1, \dots, 6$ ). In the present approach each relevant interatomic interaction is associated with a  $U_i(2)$  algebra. The operators in the model are expressed in terms of the generators of these algebras, and the symmetry requirements of the tetrahedral group  $\mathcal{T}_d$  can be readily imposed [14, 24]. The local operators  $\{\hat{G}_i\}$  acting on bond  $i$  can be projected to any of the fundamental irreps  $\Gamma = A_1, E$  and  $F_2$ . Using the  $\hat{J}_{\mu,i}$  generators we obtain the  $\mathcal{T}_d$  tensors

$$\hat{T}_{\mu,\gamma}^\Gamma = \sum_{i=1}^6 \alpha_{\gamma,i}^\Gamma \hat{J}_{\mu,i} , \quad (12)$$

where  $\mu = \pm, 0$  and  $\gamma$  denotes the component of  $\Gamma$ . The explicit expressions are given by

$$\hat{T}_{\mu,1}^{A_1} = \frac{1}{\sqrt{6}} \sum_{i=1}^6 \hat{J}_{\mu,i} ,$$

$$\begin{aligned}
\hat{T}_{\mu,1}^E &= \frac{1}{2\sqrt{3}} \left( \hat{J}_{\mu,1} + \hat{J}_{\mu,2} - 2\hat{J}_{\mu,3} + \hat{J}_{\mu,4} - 2\hat{J}_{\mu,5} + \hat{J}_{\mu,6} \right) , \\
\hat{T}_{\mu,2}^E &= \frac{1}{2} \left( \hat{J}_{\mu,1} - \hat{J}_{\mu,2} - \hat{J}_{\mu,4} + \hat{J}_{\mu,6} \right) , \\
\hat{T}_{\mu,1}^{F_2} &= \frac{1}{\sqrt{2}} \left( \hat{J}_{\mu,1} - \hat{J}_{\mu,6} \right) , \\
\hat{T}_{\mu,2}^{F_2} &= \frac{1}{\sqrt{2}} \left( \hat{J}_{\mu,2} - \hat{J}_{\mu,4} \right) , \\
\hat{T}_{\mu,3}^{F_2} &= \frac{1}{\sqrt{2}} \left( \hat{J}_{\mu,3} - \hat{J}_{\mu,5} \right) .
\end{aligned} \tag{13}$$

The Hamiltonian operator can be constructed by repeated couplings of these tensors to a total symmetry  $A_1$ , since it must commute with all operations in  $\mathcal{T}_d$  [14].

All calculations are carried out in a symmetry-adapted basis, which is projected from the local basis

$$\begin{array}{ccccccc}
U_1(2) & \otimes & \cdots & \otimes & U_6(2) & \supset & SO_1(2) \otimes \cdots \otimes SO_6(2) \supset SO(2) \\
\downarrow & & & & \downarrow & & \downarrow \\
| [N_1] & , & \cdots & , & [N_6] & ; & v_1 , \cdots , v_6 ; V \rangle
\end{array} \tag{14}$$

in which each anharmonic oscillator is well defined. By symmetry considerations,  $N_i = N$  for the six oscillators,  $v_i = N_i/2 - m_i$  denotes the number of quanta in bond  $i$  and  $V = \sum_i v_i$  is the total number of quanta. The local basis states for each oscillator are usually written as  $|N_i, v_i\rangle$ , where  $v_i = (N_i - 2m_i)/2 = 0, 1, \dots, [N_i/2]$  denotes the number of oscillator quanta in the  $i$ -th oscillator. The states with one quantum  $V = 1$  are denoted by  $|i\rangle$  with  $v_i = 1$  and  $v_{j \neq i} = 0$ . Using the same projection technique as for the generators (13), we find the six fundamental modes

$$|{}^1\phi_\gamma^\Gamma\rangle = \sum_{i=1}^6 \alpha_{\gamma,i}^\Gamma |i\rangle . \tag{15}$$

The expansion coefficients are the same as in Eq. (13). The states with a higher number of quanta  $|{}^V\phi_\gamma^\Gamma\rangle$  can be constructed using the Clebsch-Gordan coefficients of  $\mathcal{T}_d$  [14, 24]. Since all operators are expressed in terms of powers of the  $U_i(2)$  generators, their matrix elements can be easily evaluated in closed form. The symmetry-adapted operators of Eq. (13) and symmetry-adapted basis states are the building blocks of the model.

We now proceed to explicitly construct the  $\text{Be}_4$  Hamiltonian. For interactions that are at most quadratic in the generators the procedure yields

$$\hat{H}_0 = \omega_1 \hat{\mathcal{H}}_{A_1} + \omega_2 \hat{\mathcal{H}}_E + \omega_3 \hat{\mathcal{H}}_{F_2} + \alpha_2 \hat{\mathcal{V}}_E + \alpha_3 \hat{\mathcal{V}}_{F_2} , \tag{16}$$

with

$$\begin{aligned}
\hat{\mathcal{H}}_\Gamma &= \frac{1}{2N} \sum_\gamma \left( \hat{T}_{-, \gamma}^\Gamma \hat{T}_{+, \gamma}^\Gamma + \hat{T}_{+, \gamma}^\Gamma \hat{T}_{-, \gamma}^\Gamma \right) , \\
\hat{\mathcal{V}}_\Gamma &= \frac{1}{N} \sum_\gamma \hat{T}_{0, \gamma}^\Gamma \hat{T}_{0, \gamma}^\Gamma .
\end{aligned} \tag{17}$$

Note that we have not included  $\hat{\mathcal{V}}_{A_1}$  in  $\hat{H}_0$ , since the combination

$$\sum_\Gamma \left( \hat{\mathcal{H}}_\Gamma + \hat{\mathcal{V}}_\Gamma \right) = \frac{1}{4N} \sum_{i=1}^6 \hat{N}_i (\hat{N}_i + 2) , \tag{18}$$

is a constant  $3(N+2)/2$ . The five interaction terms in Eq. (16) correspond to linear combinations of the Casimir operators of [14]. However, for a good description of the vibrational energies of  $\text{Be}_4$  it is

necessary to include interactions which are related to the vibrational angular momenta associated with the degenerate modes  $E$  and  $F_2$ . These kind of terms is absent in the former versions of the model [12, 14]. We now proceed to show how they can be obtained in the present formalism. In configuration space the vibrational angular momentum operator for the  $E$  mode is given by [25]

$$\hat{l}^{A_2} = -i \left( q_1^E \frac{\partial}{\partial q_2^E} - q_2^E \frac{\partial}{\partial q_1^E} \right), \quad (19)$$

where  $q_1^E$  and  $q_2^E$  are the normal coordinates associated to the  $E$  mode. This relation can be transformed to the algebraic space by means of the harmonic oscillator operators

$$b_\gamma^{\Gamma\dagger} = \frac{1}{\sqrt{2}} \left( q_\gamma^\Gamma - \frac{\partial}{\partial q_\gamma^\Gamma} \right), \quad b_\gamma^\Gamma = \frac{1}{\sqrt{2}} \left( q_\gamma^\Gamma + \frac{\partial}{\partial q_\gamma^\Gamma} \right), \quad (20)$$

to obtain

$$\hat{l}^{A_2} = -i \left( b_1^{E\dagger} b_2^E - b_2^{E\dagger} b_1^E \right). \quad (21)$$

Here  $b_\gamma^E = \sum_i \alpha_{\gamma,i}^E b_i$ , with a similar form for  $b_\gamma^{\Gamma\dagger}$ , while the  $\alpha_{\gamma,i}^E$  can be read from Eqs. (12,13). In order to find the algebraic expression for  $\hat{l}^{A_2}$  we first introduce a scale transformation

$$\bar{b}_i^\dagger \equiv \hat{J}_{-,i}/\sqrt{N_i}, \quad \bar{b}_i \equiv \hat{J}_{+,i}/\sqrt{N_i}. \quad (22)$$

The relevant commutator can then be expressed as

$$[\bar{b}_i, \bar{b}_i^\dagger] = \frac{1}{N_i} [\hat{J}_{+,i}, \hat{J}_{-,i}] = \frac{1}{N_i} 2\hat{J}_{0,i} = 1 - \frac{2\hat{v}_i}{N_i}, \quad (23)$$

where

$$\hat{v}_i = \frac{\hat{N}_i}{2} - \hat{J}_{0,i}. \quad (24)$$

The other two commutation relations of Eq. (11) are not modified by the scale transformation of Eq. (22). In the harmonic limit, which is defined by  $N_i \rightarrow \infty$ , Eq. (23) reduces to the standard boson commutator  $[\bar{b}_i, \bar{b}_i^\dagger] = 1$ . This limit corresponds to a contraction of  $SU(2)$  to the Weyl algebra and can be used to obtain a geometric interpretation of algebraic operators in terms of those in configuration space. In the opposite sense, Eq. (22) provides a procedure to construct the anharmonic representation of harmonic operators through the correspondence  $b_i^\dagger \rightarrow \bar{b}_i^\dagger = \hat{J}_{-,i}/\sqrt{N_i}$  and  $b_i \rightarrow \bar{b}_i = \hat{J}_{+,i}/\sqrt{N_i}$ . Applying this method to the vibrational angular momentum we find

$$\hat{l}^{A_2} = -\frac{i}{N} \left( \hat{T}_{-,1}^E \hat{T}_{+,2}^E - \hat{T}_{-,2}^E \hat{T}_{+,1}^E \right). \quad (25)$$

For the vibrational angular momentum  $\hat{l}_\gamma^{F_1}$  associated with the  $F_2$  mode we find a similar expression. The corresponding interactions are

$$\hat{H}_1 = g_{22} \hat{l}^{A_2} \hat{l}^{A_2} + g_{33} \sum_\gamma \hat{l}_\gamma^{F_1} \hat{l}_\gamma^{F_1}. \quad (26)$$

With this method we obtain an algebraic realization of arbitrary configuration space interactions. As a simple example, a one-dimensional harmonic oscillator Hamiltonian  $\hat{H}_i = (b_i^\dagger b_i + b_i b_i^\dagger)/2$ , transforms into

$$\frac{1}{2N} (\hat{J}_{-,i} \hat{J}_{+,i} + \hat{J}_{+,i} \hat{J}_{-,i}) = \frac{1}{N} (\hat{J}_i^2 - \hat{J}_{0,i}^2) = \hat{v}_i + 1/2 - \frac{\hat{v}_i^2}{N}, \quad (27)$$

where in the last step we used Eq. (24). The spectrum of Eq. (27) has an anharmonic correction, analogous to the quadratic term in the Morse potential spectrum. We are thus substituting harmonic oscillators by Morse oscillators.

A more interesting application is to use our model to fit the spectroscopic data of several polyatomic molecules. In the case of  $\text{Be}_4$  the energy spectrum was analyzed by *ab initio* methods in [17], where force-field constants corresponding to an expansion of the potential up to fourth order in the normal coordinates and momenta were evaluated. We have generated the *ab initio* spectrum up to three quanta using the analysis in [25]. For the algebraic Hamiltonian we take [16]

$$\begin{aligned} \hat{H} = & \omega_1 \hat{\mathcal{H}}_{A_1} + \omega_2 \hat{\mathcal{H}}_E + \omega_3 \hat{\mathcal{H}}_{F_2} + X_{12} \left( \hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_E \right) + X_{13} \left( \hat{\mathcal{H}}_{A_1} \hat{\mathcal{H}}_{F_2} \right) + X_{33} \left( \hat{\mathcal{H}}_{F_2} \right)^2 \\ & + g_{33} \sum_{\gamma} \hat{l}_{\gamma}^{F_1} \hat{l}_{\gamma}^{F_1} + t_{33} \hat{\mathcal{O}}_{33} + t_{23} \hat{\mathcal{O}}_{23} , \end{aligned} \quad (28)$$

The terms  $\hat{\mathcal{O}}_{33}$  and  $\hat{\mathcal{O}}_{23}$  represent the algebraic form of the corresponding interactions in [25] which are responsible for the splitting of the vibrational levels in the  $(\nu_1, \nu_2^m, \nu_3^l) = (0, 0^0, 2^2)$  and the  $(0, 1^1, 1^1)$  overtones [16].

In Table I we show the results of a least-square fit to the vibrational energies of  $\text{Be}_4$  with the Hamiltonian of Eq. (28). The r.m.s. deviation obtained is  $2.6 \text{ cm}^{-1}$ , which can be considered of spectroscopic quality. We point out that in [25, 26] several higher order interactions are present which we have neglected. Since our model can be put into a one to one correspondence with the configuration space calculations, it is in fact possible to improve the accuracy of the fit considerably, but we have used a simpler Hamiltonian than the one of [25, 26]. When no *ab initio* calculations are available (or feasible) the present approach can be used empirically, achieving increasingly good fits by the inclusion of higher order interactions [16].

We note that the  $\text{Be}_4$  Hamiltonian of Eq. (28) preserves the total number of quanta  $V$ . This is a good approximation for this case according to the analysis of [25, 26], but it is known that Fermi resonances can occur for certain molecules when the fundamental mode frequencies are such that  $(V, V')$  states with  $V \neq V'$  are close in energy. These interactions can be introduced in the Hamiltonian but the size of the energy matrices grows very rapidly, so the best way to deal with this problem is through perturbation theory.

## 4 $\mathcal{D}_{3h}$ triatomic molecules

For  $\mathcal{D}_{3h}$  molecules we follow a similar procedure, namely, we construct the  $\mathcal{D}_{3h}$  symmetry-adapted operators and states analogous to Eq. (13,15) and carry out the building up procedure to construct the Hamiltonian and states with a higher number of quanta with the appropriate projection operators and Clebsch-Gordan coefficients [19].

In Table II we present the fits to the spectra of  $\text{Be}_3$ ,  $\text{Na}_3^+$  and  $\text{H}_3^+$  up to three quanta. While remarkably accurate descriptions of the first two molecules can be achieved using a four-parameter Hamiltonian, we were forced to include four additional higher order terms in the  $\text{H}_3^+$  Hamiltonian in order to properly describe this molecule. This is in accordance with the work of Carter and Meyer [18], who were forced to include twice as many terms in the potential energy surface for  $\text{H}_3^+$  than for the  $\text{Na}_3^+$  molecule. The  $\text{H}_3^+$  ion is a very “soft” molecule which, due to the light mass of its atomic constituents carries out large amplitude oscillations from its equilibrium positions [18].

## 5 The methane molecule

We now turn our attention to the  $\text{CH}_4$  molecule, for which we shall make a detailed description. For methane we have four  $U(2)$  algebras corresponding to the C-H interactions and six more representing the

H-H couplings. The assignments and the choice of the Cartesian coordinate system are the same as in [14]. The molecular dynamical group is then given by the product

$$\mathcal{G} = U_1(2) \otimes U_2(2) \otimes \dots \otimes U_{10}(2) . \quad (29)$$

The labeling is such that  $i = 1, \dots, 4$  correspond to the C-H couplings while the other values of  $i$  are associated with H-H interactions. Consequently there are two different boson numbers,  $N_s$  for the C-H couplings and  $N_b$  for the H-H couplings, which correspond to the stretching and bending modes, respectively. The tetrahedral symmetry of methane is taken into account by projecting the local operators  $\{\hat{G}_i\}$ , which act on bond  $i$ , on the irreducible representations  $\Gamma$  of the tetrahedral group  $\mathcal{T}_d$ . The explicit expressions for the  $\mathcal{T}_d$  tensors for the stretching modes are

$$\begin{aligned} \hat{T}_{\mu,1}^{A_{1,s}} &= \frac{1}{2} \sum_{i=1}^4 \hat{J}_{\mu,i} , \\ \hat{T}_{\mu,1}^{F_{2,s}} &= \frac{1}{2} (\hat{J}_{\mu,1} - \hat{J}_{\mu,2} + \hat{J}_{\mu,3} - \hat{J}_{\mu,4}) , \\ \hat{T}_{\mu,2}^{F_{2,s}} &= \frac{1}{2} (\hat{J}_{\mu,1} - \hat{J}_{\mu,2} - \hat{J}_{\mu,3} + \hat{J}_{\mu,4}) , \\ \hat{T}_{\mu,3}^{F_{2,s}} &= \frac{1}{2} (\hat{J}_{\mu,1} + \hat{J}_{\mu,2} - \hat{J}_{\mu,3} - \hat{J}_{\mu,4}) , \end{aligned} \quad (30)$$

while for the bending modes we have

$$\begin{aligned} \hat{T}_{\mu,1}^{A_{1,b}} &= \frac{1}{\sqrt{6}} \sum_{i=5}^{10} \hat{J}_{\mu,i} , \\ \hat{T}_{\mu,1}^{E_b} &= \frac{1}{2\sqrt{3}} (\hat{J}_{\mu,5} + \hat{J}_{\mu,6} - 2\hat{J}_{\mu,7} + \hat{J}_{\mu,8} - 2\hat{J}_{\mu,9} + \hat{J}_{\mu,10}) , \\ \hat{T}_{\mu,2}^{E_b} &= \frac{1}{2} (\hat{J}_{\mu,5} - \hat{J}_{\mu,6} - \hat{J}_{\mu,8} + \hat{J}_{\mu,10}) , \\ \hat{T}_{\mu,1}^{F_{2,b}} &= \frac{1}{\sqrt{2}} (\hat{J}_{\mu,5} - \hat{J}_{\mu,10}) , \\ \hat{T}_{\mu,2}^{F_{2,b}} &= \frac{1}{\sqrt{2}} (\hat{J}_{\mu,6} - \hat{J}_{\mu,8}) , \\ \hat{T}_{\mu,3}^{F_{2,b}} &= \frac{1}{\sqrt{2}} (\hat{J}_{\mu,7} - \hat{J}_{\mu,9}) . \end{aligned} \quad (31)$$

As before, the algebraic Hamiltonian can be constructed by repeated couplings of these tensors to a total symmetry  $A_1$ .

The methane molecule has nine vibrational degrees of freedom. Four of them correspond to the fundamental stretching modes ( $A_1 \oplus F_2$ ) and the other five to the fundamental bending modes ( $E \oplus F_2$ ) [27]. The projected tensors of Eqs. (30) and (31) correspond to ten degrees of freedom, four of which ( $A_1 \oplus F_2$ ) are related to stretching modes and six ( $A_1 \oplus E \oplus F_2$ ) to the bendings. Consequently we can identify the tensor  $\hat{T}_{\mu,1}^{A_{1,b}}$  as the operator associated to a spurious mode. This identification makes it possible to eliminate the spurious states *exactly*. This is achieved by (i) ignoring the  $\hat{T}_{\mu,1}^{A_{1,b}}$  tensor in the construction of the Hamiltonian, and (ii) diagonalizing this Hamiltonian in a symmetry-adapted basis from which the spurious mode has been removed following the procedure of [14]. We note that the condition on the Hamiltonian that was used in [14] to exclude the spurious contributions, does not automatically hold for states with higher number of quanta.

According to the above procedure, we now construct the  $\mathcal{T}_d$  invariant interactions that are at most quadratic in the generators and conserve the total number of quanta

$$\hat{\mathcal{H}}_{\Gamma_x} = \frac{1}{2N_x} \sum_{\gamma} \left( \hat{T}_{-, \gamma}^{\Gamma_x} \hat{T}_{+, \gamma}^{\Gamma_x} + \hat{T}_{+, \gamma}^{\Gamma_x} \hat{T}_{-, \gamma}^{\Gamma_x} \right) ,$$

$$\hat{\mathcal{V}}_{\Gamma_x} = \frac{1}{N_x} \sum_{\gamma} \hat{T}_{0,\gamma}^{\Gamma_x} \hat{T}_{0,\gamma}^{\Gamma_x} . \quad (32)$$

Here  $\Gamma = A_1, F_2$  for the stretching vibrations  $x = s$  and  $\Gamma = E, F_2$  for the bending vibrations  $x = b$ . In addition there are two stretching-bending interactions

$$\begin{aligned} \hat{\mathcal{H}}_{sb} &= \frac{1}{2\sqrt{N_s N_b}} \sum_{\gamma} \left( \hat{T}_{-, \gamma}^{F_{2,s}} \hat{T}_{+, \gamma}^{F_{2,b}} + \hat{T}_{+, \gamma}^{F_{2,s}} \hat{T}_{-, \gamma}^{F_{2,b}} \right) , \\ \hat{\mathcal{V}}_{sb} &= \frac{1}{\sqrt{N_s N_b}} \sum_{\gamma} \hat{T}_{0,\gamma}^{F_{2,s}} \hat{T}_{0,\gamma}^{F_{2,b}} . \end{aligned} \quad (33)$$

The zeroth order vibrational Hamiltonian is now written as

$$\begin{aligned} \hat{H}_0 &= \omega_1 \hat{\mathcal{H}}_{A_{1,s}} + \omega_2 \hat{\mathcal{H}}_{E_b} + \omega_3 \hat{\mathcal{H}}_{F_{2,s}} + \omega_4 \hat{\mathcal{H}}_{F_{2,b}} + \omega_{34} \hat{\mathcal{H}}_{sb} \\ &\quad + \alpha_2 \hat{\mathcal{V}}_{E_b} + \alpha_3 \hat{\mathcal{V}}_{F_{2,s}} + \alpha_4 \hat{\mathcal{V}}_{F_{2,b}} + \alpha_{34} \hat{\mathcal{V}}_{sb} . \end{aligned} \quad (34)$$

The interaction  $\hat{\mathcal{V}}_{A_{1,s}}$  has not been included since, in analogy to Eq. (18), the combination

$$\sum_{\Gamma} \left( \hat{\mathcal{H}}_{\Gamma_s} + \hat{\mathcal{V}}_{\Gamma_s} \right) = \frac{1}{4N_s} \sum_{i=1}^4 \hat{N}_i (\hat{N}_i + 2) , \quad (35)$$

corresponds to a constant  $N_s + 2$ . A similar relation holds for the bending interactions, but in this case the interaction  $\hat{\mathcal{V}}_{A_{1,b}}$  has already been excluded in order to remove the spurious  $A_1$  bending mode. The subscripts of the parameters correspond to the  $(\nu_1, \nu_2^{l_2}, \nu_3^{l_3}, \nu_4^{l_4})$  labeling of a set of basis states for the vibrational levels of  $\text{CH}_4$ . Here  $\nu_1, \nu_2, \nu_3$  and  $\nu_4$  denote the number of quanta in the  $A_{1,s}, E_b, F_{2,s}$  and  $F_{2,b}$  modes, respectively. The labels  $l_i$  are related to the vibrational angular momentum associated with degenerate vibrations. The allowed values are  $l_i = \nu_i, \nu_i - 2, \dots, 1$  or  $0$  for  $\nu_i$  odd or even [27].

In the harmonic limit the interactions of Eqs. (32) and (33) again attain a particularly simple form, which can be directly related to configuration space interactions. This limit is obtained, as before, by rescaling  $\hat{J}_{+,i}$  and  $\hat{J}_{-,i}$  by  $\sqrt{N_i}$  and taking  $N_i \rightarrow \infty$ , so that

$$\begin{aligned} \lim_{N_i \rightarrow \infty} \frac{\hat{J}_{+,i}}{\sqrt{N_i}} &= b_i , \\ \lim_{N_i \rightarrow \infty} \frac{\hat{J}_{-,i}}{\sqrt{N_i}} &= b_i^{\dagger} , \\ \lim_{N_i \rightarrow \infty} \frac{1}{N_i} [\hat{J}_{+,i}, \hat{J}_{-,i}] &= \lim_{N_i \rightarrow \infty} \frac{2\hat{J}_{0,i}}{N_i} = 1 . \end{aligned} \quad (36)$$

where the operators  $b_i$  and  $b_j^{\dagger}$  satisfy the standard boson commutation relation  $[b_i, b_j^{\dagger}] = \delta_{ij}$ . Applying the harmonic limit to the interactions of Eqs. (32) and (33) we obtain

$$\begin{aligned} \lim_{N_x \rightarrow \infty} \hat{\mathcal{H}}_{\Gamma_x} &= \frac{1}{2} \sum_{\gamma} \left( b_{\gamma}^{\Gamma_x \dagger} b_{\gamma}^{\Gamma_x} + b_{\gamma}^{\Gamma_x} b_{\gamma}^{\Gamma_x \dagger} \right) , \\ \lim_{N_x \rightarrow \infty} \hat{\mathcal{V}}_{\Gamma_x} &= 0 , \\ \lim_{N_s, N_b \rightarrow \infty} \hat{\mathcal{H}}_{sb} &= \frac{1}{2} \sum_{\gamma} \left( b_{\gamma}^{F_{2,s} \dagger} b_{\gamma}^{F_{2,b}} + b_{\gamma}^{F_{2,s}} b_{\gamma}^{F_{2,b} \dagger} \right) , \\ \lim_{N_s, N_b \rightarrow \infty} \hat{\mathcal{V}}_{sb} &= 0 . \end{aligned} \quad (37)$$

Here the operators  $b_{\gamma}^{\Gamma_x \dagger}$  are given in terms of the local boson operators  $b_i^{\dagger}$  through the coefficients  $\alpha_{\gamma,i}^{\Gamma_x}$  given in Eqs. (30,31)

$$b_{\gamma}^{\Gamma_x \dagger} = \sum_{i=1}^{10} \alpha_{\gamma,i}^{\Gamma_x} b_i^{\dagger}, \quad (38)$$

with a similar relation for the annihilation operators. From Eq. (37) the physical interpretation of the interactions is immediate. The  $\hat{\mathcal{H}}_{\Gamma_x}$  terms represent the anharmonic counterpart of the harmonic interactions, while the  $\hat{\mathcal{V}}_{\Gamma_x}$  terms are purely anharmonic contributions which vanish in the harmonic limit. In an application to the ozone molecule it was found that these terms can account for the strong anharmonicities and incorporate the effect of Darling-Dennison type couplings [20].

The zeroth order Hamiltonian of Eq. (34) is not sufficient to obtain a high-quality fit of the vibrations of methane. Several physically meaningful interaction terms that are essential for such a fit are not present in Eq. (34). They arise in our model as higher order interactions. It is an advantage of the symmetry-adapted model that the various interaction terms have a direct physical interpretation and a specific action on the various modes [16]. Hence the addition of higher order terms and anharmonicities can be done in a systematic way. For the study of the vibrational excitations of methane we use the  $\mathcal{T}_d$  invariant Hamiltonian [21]

$$\begin{aligned} \hat{H} = & \omega_1 \hat{\mathcal{H}}_{A_{1,s}} + \omega_2 \hat{\mathcal{H}}_{E_b} + \omega_3 \hat{\mathcal{H}}_{F_{2,s}} + \omega_4 \hat{\mathcal{H}}_{F_{2,b}} + \alpha_3 \hat{\mathcal{V}}_{F_{2,s}} \\ & + X_{11} \left( \hat{\mathcal{H}}_{A_{1,s}} \right)^2 + X_{22} \left( \hat{\mathcal{H}}_{E_b} \right)^2 + X_{33} \left( \hat{\mathcal{H}}_{F_{2,s}} \right)^2 + X_{44} \left( \hat{\mathcal{H}}_{F_{2,b}} \right)^2 \\ & + X_{12} \left( \hat{\mathcal{H}}_{A_{1,s}} \hat{\mathcal{H}}_{E_b} \right) + X_{14} \left( \hat{\mathcal{H}}_{A_{1,s}} \hat{\mathcal{H}}_{F_{2,b}} \right) \\ & + X_{23} \left( \hat{\mathcal{H}}_{E_b} \hat{\mathcal{H}}_{F_{2,s}} \right) + X_{24} \left( \hat{\mathcal{H}}_{E_b} \hat{\mathcal{H}}_{F_{2,b}} \right) + X_{34} \left( \hat{\mathcal{H}}_{F_{2,s}} \hat{\mathcal{H}}_{F_{2,b}} \right) \\ & + g_{22} \left( \hat{l}^{A_2} \right)^2 + g_{33} \sum_{\gamma} \hat{l}_{s,\gamma}^{F_1} \hat{l}_{s,\gamma}^{F_1} + g_{44} \sum_{\gamma} \hat{l}_{b,\gamma}^{F_1} \hat{l}_{b,\gamma}^{F_1} + g_{34} \sum_{\gamma} \hat{l}_{s,\gamma}^{F_1} \hat{l}_{b,\gamma}^{F_1} \\ & + t_{33} \hat{\mathcal{O}}_{ss} + t_{44} \hat{\mathcal{O}}_{bb} + t_{34} \hat{\mathcal{O}}_{sb} + t_{23} \hat{\mathcal{O}}_{2s} + t_{24} \hat{\mathcal{O}}_{2b}. \end{aligned} \quad (39)$$

The interpretation of the  $\omega_i$  and  $\alpha_3$  terms follows from Eq. (37). The  $X_{ij}$  terms are quadratic in the operators  $\hat{\mathcal{H}}_{\Gamma_x}$  and hence represent anharmonic vibrational interactions. The  $g_{ij}$  terms are related to the vibrational angular momenta associated with the degenerate vibrations. As mentioned before, these interactions, which are fundamental to describe molecular systems with a high degree of symmetry, are absent in previous versions of the vibron model in which the interaction terms are expressed in terms of Casimir operators and products thereof [12, 14]. They give rise to a splitting of vibrational levels with the same values of  $(\nu_1, \nu_2, \nu_3, \nu_4)$  but with different  $l_2, l_3$  and/or  $l_4$ . Their algebraic realization is given by

$$\begin{aligned} \hat{l}^{A_2} &= -i \sqrt{2} \frac{1}{N_b} [\hat{T}_{-}^{E_b} \times \hat{T}_{+}^{E_b}]^{A_2}, \\ \hat{l}_{x,\gamma}^{F_1} &= +i \sqrt{2} \frac{1}{N_x} [\hat{T}_{-}^{F_{2,x}} \times \hat{T}_{+}^{F_{2,x}}]_{\gamma}^{F_1}. \end{aligned} \quad (40)$$

The square brackets in Eq. (40) denote the tensor coupling under the point group  $\mathcal{T}_d$

$$[\hat{T}^{\Gamma_1} \times \hat{T}^{\Gamma_2}]_{\gamma}^{\Gamma} = \sum_{\gamma_1, \gamma_2} C(\Gamma_1, \Gamma_2, \Gamma; \gamma_1, \gamma_2, \gamma) \hat{T}_{\gamma_1}^{\Gamma_1} \hat{T}_{\gamma_2}^{\Gamma_2}, \quad (41)$$

where the expansion coefficients are the Clebsch-Gordan coefficients for  $\mathcal{T}_d$  [14, 24]. In the harmonic limit the expectation value of the diagonal terms in Eq. (39) leads to the familiar Dunham expansion [27]

$$\sum_i \omega_i \left( v_i + \frac{d_i}{2} \right) + \sum_{j \geq i} \sum_i X_{ij} \left( v_i + \frac{d_i}{2} \right) \left( v_j + \frac{d_j}{2} \right) + \sum_{j \geq i} \sum_i g_{ij} l_i l_j. \quad (42)$$

Here  $d_i$  is the degeneracy of the vibration. The  $t_{ij}$  terms in Eq. (39) give rise to further splittings of the vibrational levels  $(\nu_1, \nu_2, \nu_3, \nu_4)$  into its possible sublevels. They can be expressed in terms of the tensor operators of Eqs. (30) and (31) as

$$\begin{aligned}\hat{\mathcal{O}}_{xy} &= \frac{1}{N_x N_y} \left( 6 \sum_{\gamma} [\hat{T}_-^{F_2, x} \times \hat{T}_-^{F_2, y}]_{\gamma}^E [\hat{T}_+^{F_2, y} \times \hat{T}_+^{F_2, x}]_{\gamma}^E - 4 \sum_{\gamma} [\hat{T}_-^{F_2, x} \times \hat{T}_-^{F_2, y}]_{\gamma}^{F_2} [\hat{T}_+^{F_2, y} \times \hat{T}_+^{F_2, x}]_{\gamma}^{F_2} \right), \\ \hat{\mathcal{O}}_{2x} &= \frac{1}{N_b N_x} \left( 8 \sum_{\gamma} [\hat{T}_-^{E_b} \times \hat{T}_-^{F_2, x}]_{\gamma}^{F_1} [\hat{T}_+^{E_b} \times \hat{T}_+^{F_2, x}]_{\gamma}^{F_1} - 8 \sum_{\gamma} [\hat{T}_-^{E_b} \times \hat{T}_-^{F_2, x}]_{\gamma}^{F_2} [\hat{T}_+^{E_b} \times \hat{T}_+^{F_2, x}]_{\gamma}^{F_2} \right). \quad (43)\end{aligned}$$

In the harmonic limit the  $t_{ij}$  terms have the same interpretation as in [25]. The  $\hat{\mathcal{O}}_{ss}$ ,  $\hat{\mathcal{O}}_{bb}$  and  $\hat{\mathcal{O}}_{sb}$  terms give rise to a splitting of the  $E$  and  $F_2$  vibrations belonging to the  $(\nu_1, \nu_2^{l_2}, \nu_3^{l_3}, \nu_4^{l_4}) = (0, 0^0, 2^2, 0^0)$ ,  $(0, 0^0, 0^0, 2^2)$  and  $(0, 0^0, 1^1, 1^1)$  levels, respectively. Similarly, the  $\hat{\mathcal{O}}_{2s}$  and  $\hat{\mathcal{O}}_{2b}$  terms split the  $F_1$  and  $F_2$  vibrations belonging to the  $(0, 1^1, 1^1, 0^0)$  and  $(0, 1^1, 0^0, 1^1)$  overtones, respectively.

The Hamiltonian of Eq. (39) involves 23 interaction strengths and the two boson numbers,  $N_s$  and  $N_b$ . The vibron number associated with the stretching vibrations is determined from the spectroscopic constants  $\omega_e$  and  $x_e \omega_e$  for the CH molecule to be  $N_s = 43$  [23]. The vibron number for the bending vibrations, which are far more harmonic than the stretching vibrations, is taken to be  $N_b = 150$ . We have carried out a least-square fit to the vibrational spectrum of methane including 44 experimental energies from [28]. The values of the fitted parameters are presented in the second column of Table III (Fit 1). In Table IV we compare the results of our calculation with the experimentally observed energies. All predicted levels up to  $V = 3$  quanta are included. We find an overall fit to the observed levels with a r.m.s. deviation which is an order of magnitude better than in previous studies. Whereas the r.m.s. deviations of standard vibron model studies in [14] and [29] are 12.16 and 11.61  $\text{cm}^{-1}$  for 19 energies, we find a value of 1.16  $\text{cm}^{-1}$  for 44 energies.

In order to address the importance of the  $\alpha_3$  term, which is completely anharmonic in origin and vanishes in the harmonic limit (see Eq. (37)), we have carried out a calculation without this term (Fit 2 of Table III). With one less interaction term the r.m.s. deviation increases from 1.16 to 4.49  $\text{cm}^{-1}$ . This shows the importance of the  $\alpha_3$  term to obtain an accurate description of the anharmonicities that are present in the data. Similarly, the third calculation (Fit 3) shows that, in a fit without the  $t_{ij}$  terms, the r.m.s. deviation increases from 1.16 to 7.81  $\text{cm}^{-1}$ .

In addition, we have carried out a fit in the harmonic limit ( $N_s, N_b \rightarrow \infty$ ). In this limit the  $\alpha_3$  term vanishes and the algebraic Hamiltonian of Eq. (39) reduces to the vibrational Hamiltonian of [25], the harmonic frequencies  $\omega_i$  and anharmonic constants  $X_{ij}$ ,  $g_{ij}$  and  $t_{ij}$  having the same meaning. The r.m.s. deviation increases to 20.42  $\text{cm}^{-1}$  (Fit 4). When we use the vibrational Hamiltonian of [25], which contains one additional interaction (called  $s_{34}$  in Table III) the quality of the fit does not improve. In fact, the r.m.s. deviation increases to 20.90  $\text{cm}^{-1}$  (Fit 5). The importance of the nondiagonal elements is demonstrated in a calculation (Fit 6), in which the data are fitted by the (diagonal) Dunham expansion of Eq. (42). For this case the r.m.s. deviation is 21.00  $\text{cm}^{-1}$ , almost the same value as for the other two calculations in the harmonic limit. The small differences in the parameter values and the r.m.s. deviation of Fits 4 and 6 show that, unlike for finite  $N_s$  and  $N_b$  (Fits 1 and 3), in the harmonic limit the nondiagonal contributions from the  $t_{ij}$  terms are not very important.

A comparison between the parameter values and the r.m.s. deviations of Fits 1–6 in Table III shows that the  $\alpha_3$  term and the anharmonic effects in the interaction terms of Eq. (39) can only be compensated for in part by the anharmonicity constants  $X_{ij}$ . The r.m.s. deviation increases from 1.16 to 4.49 and 20.42  $\text{cm}^{-1}$  for Fits 1, 2 and 4, respectively.

## 6 Summary and conclusions

In summary, in this paper we have studied the vibrational excitations of several molecules in a symmetry-adapted algebraic model. In particular, for the methane molecule we find an overall fit to the 44 observed

levels with a r.m.s. deviation of  $1.16\text{ cm}^{-1}$ , which can be considered of spectroscopic quality. We pointed out that for this calculation the  $\alpha_3$  term in Eq. (39) in combination with the anharmonic effects in the other interaction terms plays a crucial role in obtaining a fit of this quality. Purely anharmonic terms of this sort arise naturally in the symmetry-adapted algebraic model, but vanish in the harmonic limit. Physically, these contributions arise from the anharmonic character of the interatomic interactions, and seem to play an important role when dealing with molecular anharmonicities, especially at higher number of quanta. This conclusion is supported by our other applications of the symmetry-adapted model to the  $\text{Be}_4$  cluster [16] and the  $\text{H}_3^+$ ,  $\text{Be}_3$  and  $\text{Na}_3^+$  molecules [19], as well as our study of two isotopes of the ozone molecule [20].

These studies suggest that the symmetry-adapted algebraic model provides a numerically efficient tool to study molecular vibrations with high precision. The main difference with other methods is the use of symmetry-adapted tensors in the construction of the Hamiltonian. In this approach, the interactions can be constructed in a systematic way, each term has a direct physical interpretation, and spurious modes can be eliminated exactly. It will be important to further explore the scope and applicability of the present approach. A more extensive study of methane including rotation-vibration couplings, states with a higher number of quanta and transition intensities is in progress.

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Table I: Fit to ab initio [26] calculations for  $\text{Be}_4$ . The values of the parameters are  $\omega_1 = 636$ ,  $\omega_2 = 453$ ,  $\omega_3 = 532$ ,  $X_{33} = 44.276$ ,  $X_{12} = 4.546$ ,  $X_{13} = -2.539$ ,  $g_{33} = -15.031$ ,  $t_{33} = -1.679$  and  $t_{23} = -1.175$ . The total number of bosons is  $N = 44$ . The parameters and energies are given in  $\text{cm}^{-1}$ .

$V$	$(\nu_1, \nu_2^m, \nu_3^l)$	$\Gamma$	Ab initio $N \rightarrow \infty$	Fit $N = 44$	$V$	$(\nu_1, \nu_2^m, \nu_3^l)$	$\Gamma$	Ab initio $N \rightarrow \infty$	Fit $N = 44$
1	$(1, 0^0, 0^0)$	$A_1$	638.6	637.0	3	$(1, 0^0, 2^0)$	$A_1$	2106.8	2105.6
	$(0, 1^1, 0^0)$	$E$	453.6	455.0		$(1, 0^0, 2^2)$	$E$	2000.1	1999.8
	$(0, 0^0, 1^1)$	$F_2$	681.9	678.2			$F_2$	2056.8	2052.8
2	$(2, 0^0, 0^0)$	$A_1$	1271.0	1269.2		$(0, 3^1, 0^0)$	$E$	1341.3	1343.7
	$(1, 1^1, 0^0)$	$E$	1087.1	1087.0		$(0, 3^3, 0^0)$	$A_1$	1355.5	1352.5
	$(1, 0^0, 1^1)$	$F_2$	1312.6	1308.3			$A_2$	1355.5	1354.4
	$(0, 2^0, 0^0)$	$A_1$	898.3	901.4		$(0, 2^{0,2}, 1^1)$	$F_2$	1565.5	1565.7
	$(0, 2^2, 0^0)$	$E$	905.4	906.1			$F_2$	1584.4	1583.1
	$(0, 1^1, 1^1)$	$F_1$	1126.7	1125.1		$(0, 2^2, 1^1)$	$F_1$	1578.5	1578.0
		$F_2$	1135.5	1134.1		$(0, 1^1, 2^{0,2})$	$E$	1821.4	1821.6
	$(0, 0^0, 2^0)$	$A_1$	1484.0	1483.0			$E$	1929.5	1929.0
	$(0, 0^0, 2^2)$	$E$	1377.3	1373.9		$(0, 1^1, 2^2)$	$A_2$	1813.3	1813.1
		$F_2$	1434.1	1429.6			$A_1$	1830.8	1831.7
3	$(3, 0^0, 0^0)$	$A_1$	1897.0	1896.7			$F_2$	1874.4	1873.2
	$(2, 1^1, 0^0)$	$E$	1714.3	1714.3			$F_1$	1883.2	1883.0
	$(2, 0^0, 1^1)$	$F_2$	1937.0	1933.7		$(0, 0^0, 3^{1,3})$	$F_2$	2136.5	2134.2
	$(1, 2^0, 0^0)$	$A_1$	1526.6	1529.2			$F_2$	2327.3	2326.9
	$(1, 2^2, 0^0)$	$E$	1533.7	1532.8		$(0, 0^0, 3^3)$	$F_1$	2199.8	2197.1
	$(1, 1^1, 1^1)$	$F_1$	1752.2	1749.7			$A_1$	2256.5	2254.4
		$F_2$	1761.0	1759.8					

Table II: Least-square energy fit for the vibrational excitations of  $\text{H}_3^+$ ,  $\text{Be}_3$  and  $\text{Na}_3^+$ . The energy differences  $\Delta E = E_{th} - E_{exp}$  are given in  $\text{cm}^{-1}$ .

$V$	$(\nu_1, \nu_2^l)$	$\Gamma$	$\text{H}_3^+$ $\Delta E$	$\text{Be}_3$ $\Delta E$	$\text{Na}_3^+$ $\Delta E$
1	$(0, 1^1)$	$E$	-1.55	0.51	0.93
	$(1, 0^0)$	$A_1$	0.42	0.02	1.95
2	$(0, 2^0)$	$A_1$	7.48	-0.74	0.37
	$(0, 2^2)$	$E$	-5.69	0.17	0.84
	$(1, 1^1)$	$E$	-0.61	0.82	1.68
	$(2, 0^0)$	$A_1$	-0.11	-0.04	1.26
3	$(0, 3^1)$	$E$	-4.46	-2.05	-1.19
	$(0, 3^3)$	$A_1$	3.18	-1.23	-0.34
	$(0, 3^3)$	$A_2$	2.44	0.61	-0.33
	$(1, 2^0)$	$A_1$	0.66	1.90	-0.01
	$(1, 2^2)$	$E$	-5.00	-1.36	0.34
	$(2, 1^1)$	$E$	4.07	0.79	-0.19
	$(3, 0^0)$	$A_1$	-1.23	-1.66	-2.06
r.m.s.			5.84	1.35	1.33
Parameters			8	4	4

Table III: Parameters in  $\text{cm}^{-1}$  obtained in the fits to the vibrational energies of  $\text{CH}_4$ .

Parameter	Fit 1	Fit 2	Fit 3	Fit 4	Fit 5	Fit 6
$N_s$	43	43	43	$\infty$	$\infty$	$\infty$
$N_b$	150	150	150	$\infty$	$\infty$	$\infty$
$\omega_1$	2977.60	2966.17	2970.03	2967.40	2966.81	2969.75
$\omega_2$	1554.83	1549.96	1550.88	1558.38	1558.51	1548.30
$\omega_3$	3076.45	3076.41	3079.33	3081.34	3082.00	3060.48
$\omega_4$	1332.22	1329.52	1337.69	1337.51	1337.54	1338.64
$\alpha_3$	582.87	—	480.33	—	—	—
$X_{11}$	3.69	10.23	6.06	-21.30	-21.19	-21.59
$X_{22}$	1.30	1.32	1.37	-1.17	-1.17	-0.28
$X_{33}$	5.43	6.97	5.34	-10.79	-11.12	-7.89
$X_{44}$	-3.47	-3.64	-4.41	-6.26	-6.27	-7.26
$X_{12}$	-3.60	-0.94	-1.47	-3.39	-3.28	-2.80
$X_{13}$	—	—	—	—	—	—
$X_{14}$	-2.86	-0.49	-2.30	-3.10	-3.00	-4.48
$X_{23}$	-11.14	-8.75	-10.68	-7.97	-8.10	-3.80
$X_{24}$	1.00	0.91	2.03	-5.37	-5.37	-4.74
$X_{34}$	-5.60	-3.97	-6.50	-3.46	-3.50	-1.21
$g_{22}$	-0.46	-0.46	-0.41	0.37	0.37	-0.62
$g_{33}$	0.19	-1.23	0.25	-4.35	-4.22	-5.49
$g_{44}$	4.07	4.11	3.79	4.98	4.98	5.30
$g_{34}$	-0.65	-0.72	-0.56	-0.74	-0.87	-0.67
$t_{33}$	0.40	0.16	—	-1.25	-1.27	—
$t_{44}$	1.00	1.00	—	0.56	0.56	—
$t_{34}$	0.21	0.24	—	0.24	0.25	—
$t_{23}$	-0.39	-0.39	—	-0.39	-0.39	—
$t_{24}$	0.13	0.13	—	0.91	0.91	—
$s_{34}$	—	—	—	—	-0.11	—
r.m.s.	1.16	4.49	7.81	20.42	20.90	21.00

Table IV: Fit to vibrational excitations of CH<sub>4</sub>. The values of the parameters are given in the second column of Table III. Here  $\Delta E = E_{cal} - E_{exp}$ . The experimental energies are taken from [28]. The wave numbers are given in cm<sup>-1</sup>.

$\Gamma$	$(\nu_1, \nu_2, \nu_3, \nu_4)$	$E_{cal}$	$E_{exp}$	$\Delta E$	$\Gamma$	$(\nu_1, \nu_2, \nu_3, \nu_4)$	$E_{cal}$	$E_{exp}$	$\Delta E$
$A_1$	(1000)	2916.32	2916.48	-0.16		(0111)	5844.98		
$E$	(0100)	1533.46	1533.33	0.13		(1200)	5974.81		
$F_2$	(0001)	1309.86	1310.76	-0.90		(1011)	7147.49		
	(0010)	3018.09	3019.49	-1.40		(0021)	7303.38		
						(2100)	7315.60		
$A_1$	(0002)	2587.77	2587.04	0.73		(0120)	7479.48		
	(0200)	3063.66	3063.65	0.01		(0120)	7557.17		
	(0011)	4323.81	4322.72	1.09		(1020)	8833.05		
	(2000)	5790.13	5790	0.13	$F_1$	(0003)	3920.46	3920.50	-0.04
	(0020)	5966.57	5968.1	-1.53		(0102)	4128.38	4128.57	-0.19
$E$	(0002)	2624.14	2624.62	-0.48		(0201)	4364.39	4363.31	1.08
	(0200)	3065.22	3065.14	0.08		(0012)	5620.08		
	(0011)	4323.09	4322.15	0.94		(0012)	5630.76		
	(1100)	4446.41	4446.41	0.00		(1101)	5755.58		
	(0020)	6045.03	6043.8	1.23		(0111)	5829.79		
$F_1$	(0101)	2845.35	2846.08	-0.73		(0111)	5848.94		
	(0011)	4323.15	4322.58	0.57		(0210)	6061.57		
	(0110)	4537.57	4537.57	0.00		(1011)	7147.53		
$F_2$	(0002)	2612.93	2614.26	-1.33		(0021)	7303.29		
	(0101)	2830.61	2830.32	0.29		(0021)	7343.21		
	(1001)	4223.46	4223.46	0.00		(1110)	7361.79		
	(0011)	4321.02	4319.21	1.81		(0120)	7518.70		
	(0110)	4543.76	4543.76	0.00		(0030)	8947.65	8947.95	-0.30
	(1010)	5845.53			$F_2$	(0003)	3871.29	3870.49	0.80
	(0020)	6003.65	6004.65	-1.00		(0003)	3931.36	3930.92	0.44
						(0102)	4143.09	4142.86	0.23
$A_1$	(0003)	3909.20	3909.18	0.02		(0201)	4349.01	4348.77	0.24
	(0102)	4131.92	4132.99	-1.07		(0201)	4378.38	4379.10	-0.72
	(0300)	4595.26	4595.55	-0.29		(1002)	5523.80		
	(1002)	5498.66				(0012)	5594.92	5597.14	-2.22
	(0012)	5617.16				(0012)	5620.68		
	(0111)	5836.11				(0012)	5632.36		
	(1200)	5973.26				(1101)	5740.86		
	(1011)	7147.56				(0111)	5830.28		
	(0021)	7300.85				(0111)	5848.46		
	(0120)	7562.91				(0210)	6054.58		
	(3000)	8583.81				(0210)	6067.03		
	(1020)	8727.97				(2001)	7094.16		
	(0030)	8975.64	8975.34	0.30		(1011)	7145.84		
$A_2$	(0102)	4161.52	4161.87	-0.35		(0021)	7266.11		
	(0300)	4595.28	4595.32	-0.04		(0021)	7303.38		
	(0111)	5844.61				(0021)	7344.87		
	(0120)	7550.53				(1110)	7365.83		
$E$	(0102)	4105.22	4105.15	0.07		(0120)	7514.67		
	(0102)	4152.15	4151.22	0.93		(2010)	8594.90		
	(0300)	4592.13	4592.03	0.10		(1020)	8786.05		
	(1002)	5535.04				(0030)	8907.91	8906.78	1.13
	(0012)	5620.36				(0030)	9045.36	9045.92	-0.56
	(0111)	5836.45							